

Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts

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Abstract—The speciation of sulfur as a function of oxygen fugacity was calculated in glasses of basaltic composition saturated experimentally with either sulfide or sulfate phases. The experiments were conducted on mixtures of synthetic and natural materials equilibrated at 1300 °C and 1 GPa in a piston-cylinder apparatus. Sulfur speciation was calculated by measuring the peak shift of the sulfur $K\alpha$ radiation relative to a sulfide standard, whereas oxygen fugacity was calculated from the composition of olivine and spinel present in the assemblages. The results are consistent with sulfur being present as sulfite (S^{4+}) in addition to sulfate (S^{6+}) in oxidized melts. Therefore, sulfur speciation derived from $SK\alpha$ peak shifts should be seen as "sulfate mole fraction equivalents" ($X(S^{6+})_{eq}$). Using the data available, an empiric function:

$$X(S^{6+})_{eq} = 0.86 / (1 + \exp(2.89 - 2.23\Delta FMQ))$$

relating sulfate mole fraction equivalents and oxygen fugacity was derived. This function can be approximated by a linear function:

$$\Delta FMQ = 2.28X(S^{6+})_{eq} + 0.32$$

which could be used as an independent oxybarometer over the range in which most of the change of speciation occurs ($+0.8 \leq \Delta FMQ \leq +1.9$). Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Sulfur can be present in silicate melts as various species, most notably as sulfide (S^{2-}) and sulfate (SO_4^{2-}), and understanding the relationship between sulfur speciation and oxygen fugacity is of interest for various reasons. For example, sulfur is a significant component in gases released by volcanic activity and sulfur-rich volcanic eruptions, some of them associated with the presence of anhydrite in the erupted magmas (e.g., Pinatubo in 1991), have been linked to short-term, high-impact variations in global climate (Rampino and Ambrose, 2000). Saturation or elimination of sulfide phases (crystalline or as immiscible liquids) during magmatic evolution or partial melting dictates the behavior of chalcophile elements (e.g., Cu, Ni) and highly siderophile elements (HSE = Ru, Rh, Pd, Re, Os, Ir, Pt, Au). These elements are of interest because of their economic value as base- or precious metals (e.g., Cu, Ni, Pd, Pt, Au) or because they are used as tracers of mantle processes (e.g., Re and Os).

In relatively reduced magmas, such as those generated in midocean ridge settings, sulfur is dominantly present as sulfide. Because of this, sulfides were considered to be the dominant sulfur species in magmatic systems. However, some magmas are sufficiently oxidized for sulfur to be present as sulfate. Carroll and Rutherford (1988) used the peak shift in the sulfur $K\alpha$ radiation, determined by electron probe microanalysis (EPMA), to estimate the change in the speciation of sulfur as a function of oxygen fugacity and showed that the transition from

sulfide-dominance to sulfate-dominance occurred between FMQ and $\Delta FMQ = +2$ (FMQ: fayalite-magnetite-quartz reference buffer). Wallace and Carmichael (1994) combined the data from Carroll and Rutherford (1988) with data on natural basaltic glasses from spreading centers, seamounts, and back-arc basins to derive an expression relating the ratio between the sulfate and the sulfide mole fractions ($X(SO_4)^{2-} / X(S)^{2-}$) and fO_2 . This relationship has been used to infer the oxidation state of natural samples from calculated sulfur speciation (e.g., Métrich and Clochiatti, 1996; Gurenko and Schmincke, 1998, 2000). Matthews et al. (1999) measured sulfur speciation and oxidation state in basaltic andesites and andesites from the Lascar volcano (Chile) and compiled the available data to generate a polynomial fit relating fO_2 as a function of the sulfate mole fraction ($X(S^{6+})$). In this paper, we present new data on the speciation of sulfur in basaltic glasses from experiments with independently constrained values of oxygen fugacity. These new data are compared with existing data on sulfur speciation as a function of oxygen fugacity. The different models for the relationship between sulfur speciation and oxygen fugacity are discussed and a new empiric function relating the apparent sulfate mole fraction and fO_2 is derived. This function provides a better data fit than the function of Wallace and Carmichael (1994), has a simpler form than that of Matthews et al. (1999), and is consistent with the presence of sulfite species (S^{4+}) in silicate melts as shown by Métrich et al. (2002). This function could be used as an independent oxybarometer in oxidized basaltic melts.

2. EXPERIMENTAL AND ANALYTICAL METHODS

A summary of experimental conditions and the method for estimating sulfur speciation are described in this section. Further details of the

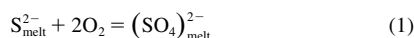
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experimental conditions and analytical methods can be found in Jugo (2003). Anhydrous experiments were conducted in an end-loaded piston-cylinder apparatus at 1300 °C and 1 GPa. Starting materials consisted of mixtures of synthetic glasses (made from mixtures of reagent-grade oxides and carbonates, fused in air), natural olivine (Fo₉₁) from West Kettle River (sample KR-37 in Canil et al., 1990), and either FeS, CaSO₄, or FeSO₄ as the source for sulfur. Mixtures were prepared to yield basaltic melts coexisting with either sulfide or sulfate and containing olivine and spinel (\pm orthopyroxene, clinopyroxene) at the run conditions. The oxidation state of the assemblages was imposed by a combination of starting and capsule materials. Graphite-lined Pt capsules imposed reducing conditions and produced sulfide-saturated assemblages regardless of the mode of sulfur addition (either as sulfide or sulfate). Capsules made of Au₈₀Pd₂₀ tubing, in combination with sulfate-bearing starting mixtures produced sulfate-saturated assemblages. The oxygen fugacity prevalent in each experiment was calculated using the oxybarometer formulation of Ballhaus et al. (1990, 1991) and the compositions of coexisting olivine and spinel crystals present as run products in the experiments. Elemental concentrations in glasses, olivine, spinel, and orthopyroxene were determined by electron probe microanalysis using a JEOL JXA-8900 probe. Typical operating conditions were 15 kV accelerating voltage and 15 nA beam current. Ferric iron in spinel was determined by stoichiometry. To provide an external check on the accuracy of Fe³⁺/ΣFe determinations from probe analyses, two natural spinel samples (KR-35 and KR-37), for which Fe³⁺/ΣFe had been previously measured by Moessbauer spectroscopy (Canil et al., 1990), were routinely analyzed. The estimated *f*O₂ obtained from our EPMA measurements of these spinels (Δ FMQ = -0.35 ± 0.52 for KR-35; Δ FMQ = -1.07 ± 0.50 for KR-37; 2σ) compare well with the *f*O₂ calculated with the Fe³⁺/ΣFe obtained by Moessbauer spectroscopy (Δ FMQ = -0.31 for KR-35; Δ FMQ = -0.86 for KR-37, Canil et al., 1990).

Sulfur speciation was measured with a technique similar to that outlined by Carroll and Rutherford (1988). A detailed scan of the peak position for the wavelength of sulfur K α radiation (ASK α) was obtained with the electron probe microanalyzer by using a pentaerythritol (PET) analyzing crystal and scanning from 535.5 pm to 538.4 pm λ (1 pm = 10⁻¹² m) with a 0.05 pm step size to cover the SK α peak and background. Operating conditions were 15 kV accelerating voltage, 60 nA beam current and 30 μ m beam diameter. Dwell time for the standards was 2 s per step. Because the noise to signal ratio is a function of sulfur concentration, longer dwell times were used for the samples. For sulfide-saturated samples (with sulfur concentration on the order of 1000 ppm), dwell times were 60 s. For sulfate-bearing samples (with sulfur concentration on the order of 1 wt%), dwell times were 30 s. The standards were analyzed repeatedly during sample analysis (every two or three samples) to monitor spectrometer drift during the sessions. Tests on several samples corroborated the change in the peak position (unrelated to spectrometer drift) with long counting times as documented in Métrich and Clochiatti (1996). To avoid this problem, samples were moved slightly under the beam ($\sim 100 \mu$ m) every 12 min.

The measured peak profiles were smoothed by averaging every three points to reduce noise. Peak positions were measured at one half of the maximum peak height relative to the background and the shift in the wavelength of SK α was measured relative to the sphalerite standard. Figure 1 illustrates typical smoothed SK α peak profiles for the barite and sphalerite standards and the difference in the peak position caused by the difference in valence.

The estimation of the sulfate mole fraction is based on the assumption that the only sulfur species present are sulfide and sulfate, which are linked through the reaction:



Because electronic configuration affects the difference in energy between orbitals, the difference in valence between S²⁻ and S⁶⁺ changes the wavelength (λ) of the K α radiation, which can be measured relative to a sulfide standard:

$$\Delta\lambda(\text{SK}\alpha)_{\text{sample}} = \lambda(\text{SK}\alpha)_{\text{sulfide standard}} - \lambda(\text{SK}\alpha)_{\text{sample}} \quad (2)$$

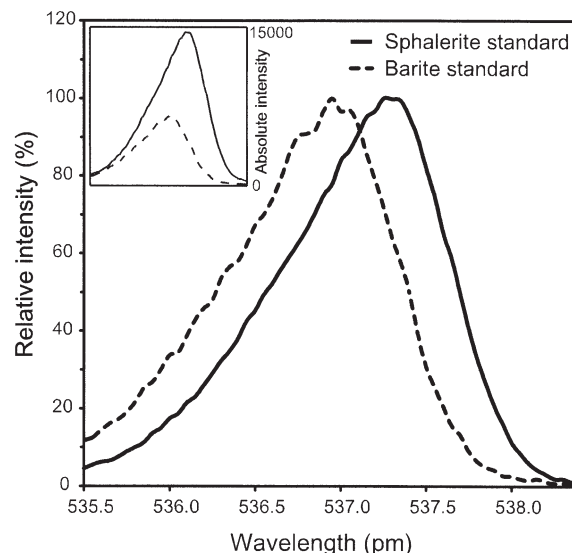


Fig. 1. Example of the SK α peak profiles measured in sphalerite and barite standards normalized to relative intensities and with background subtracted. Original profiles in absolute intensities are shown in the inset. Measurement conditions were identical for both standards; the difference in absolute intensities reflects the different proportions of sulfur in sphalerite and barite (32.9 and 13.7 wt% respectively).

Because the maximum shift in the wavelength is obtained for pure sulfates, the shift in the peak produced by a sulfate standard can be used to define a sulfate mole fraction scale:

$$X(\text{S}^{6+}) = \Delta\lambda(\text{SK}\alpha)_{\text{sample}} / \Delta\lambda(\text{SK}\alpha)_{\text{sulfate standard}} \quad (3)$$

where $X(\text{S}^{6+}) = 0$ when the sample is a sulfide, and $X(\text{S}^{6+}) = 1$ when the sample is a sulfate.

3. RESULTS

All the silicate glasses produced were basaltic in composition (Table 1) and coexisted with olivine, spinel, and a sulfur-bearing liquid phase. Orthopyroxene and clinopyroxene were present in some runs. The sulfur phases quenched to pyrrhotite or anhydrite but were present at the run conditions as either immiscible sulfide or sulfate liquids, as inferred from their rounded geometry in polished sections. Olivine was compositionally homogeneous with Fo contents ranging from 0.90 to 0.95. To verify that olivine equilibrated with the melt, we calculated the partitioning of magnesium and ferrous iron between olivine and melt (K_D , Roeder and Emslie, 1970). The ferrous iron content in the glasses was obtained by subtracting the ferric iron content (estimated using the method of Kilinc et al., 1983) from the total iron measured as FeO. The average K_D was 0.32 ± 0.4 for the sulfide-saturated runs, and 0.31 ± 0.01 for the sulfate-saturated runs. These values are consistent with the expected K_D ($K_D \approx 0.33$ at 1 GPa; Ulmer, 1989) and show that olivine was in equilibrium with the silicate melt.

The peak shift between sphalerite and barite from 22 replicate analyses on each standard is 0.304 ± 0.020 pm (2σ), which is similar to the peak shifts documented by Carroll and Rutherford (1988) (0.306 ± 0.016 pm; 2σ), Wallace and Carmichael (1994) (0.300 ± 0.006 to 0.313 ± 0.022 pm; 2σ), Métrich and Clochiatti (1996) (0.310 ± 0.020 to $0.311 \pm$

Table 1. Compositions of the glasses analyzed (wt%).

Run	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	CaO	Na ₂ O	S	Total ^a
Sulfide saturated										
52B	47.1 (6) ^b	0.70 (4)	17.7 (2)	0.07 (2)	8.7 (2)	11.9 (4)	10.8 (2)	2.21 (9)	0.16 (1)	99.6
54A	50.1 (2)	0.71 (2)	17.4 (1)	0.11 (1)	5.2 (3)	11.6 (1)	11.9 (2)	2.6 (2)	0.11 (2)	99.9
54B	50.1 (2)	0.73 (4)	18.0 (2)	0.12 (1)	5.3 (2)	11.1 (2)	11.6 (1)	2.52 (7)	0.11 (2)	99.7
Sulfate saturated										
26	45.6 (3)	0.61 (4)	15.5 (1)	0.02 (1)	8.2 (1)	12.8 (2)	12.6 (2)	1.76 (7)	1.28 (9)	100.3
30B	45.2 (3)	0.60 (4)	16.5 (2)	0.01 (1)	8.1 (2)	12.0 (2)	10.6 (3)	3.0 (6)	1.52 (3)	99.8
34	46.3 (7)	0.59 (3)	16.2 (4)	0.04 (2)	7.9 (3)	12.9 (2)	11.3 (4)	2.1 (4)	1.0 (2)	99.8
35A	46.5 (3)	0.53 (3)	15.3 (2)	0.07 (1)	7.5 (2)	14.8 (2)	9.6 (2)	1.84 (8)	1.6 (2)	100.1
50	44.1 (5)	0.59 (3)	15.5 (2)	0.03 (1)	8.0 (3)	13.2 (3)	12.5 (1)	1.81 (8)	1.62 (4)	99.8
52A	43.5 (3)	0.58 (1)	14.7 (2)	0.02 (1)	11.4 (2)	13.8 (3)	9.2 (1)	1.91 (5)	1.80 (3)	99.6
56A	46.2 (3)	0.57 (3)	15.2 (1)	0.08 (1)	7.9 (1)	15.6 (1)	9.7 (1)	2.05 (6)	1.15 (8)	100.2
56B	45.8 (2)	0.56 (2)	15.0 (1)	0.09 (2)	7.9 (1)	15.9 (2)	9.6 (1)	2.00 (6)	1.26 (6)	100.0

^a Totals are calculated with S as SO₃.

^b Numbers in parentheses are standard deviations (1 σ) on the last significant figure.

0.018 pm; 2 σ), and Gurenko and Schmincke (1998, 2000) (0.304 \pm 0.014 to 0.309 \pm 0.018 pm; 2 σ).

The shift in SK α was measured in glasses from three sulfide-saturated and eight sulfate-saturated experiments. In general, the samples show shifts similar to those of the sphalerite and barite standards (Fig. 2). The results are summarized in Table 2 and plotted against calculated oxidation state in Figure 3. The uncertainties shown include the propagated errors associated with the peak shift between the standards (\pm 0.020 pm, 2 σ) and the 2 σ uncertainties of the oxybarometer (\pm 0.8 log units above FMQ, and \pm 2.4 log units near Δ FMQ = -3, Ballhaus et al., 1991). The absence of orthopyroxene in some runs would produce a shift in the Δ FMQ values of less than 0.2 log units (Ballhaus et al., 1991)

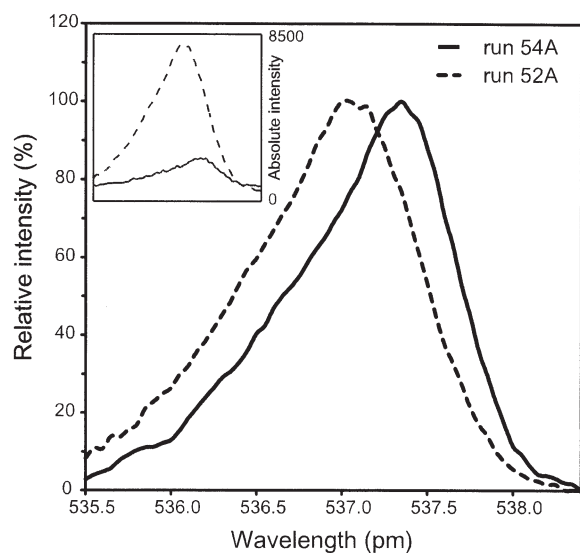


Fig. 2. Example of the SK α peak profiles measured in experimental glasses. Runs 54A (solid line) and 52A (dashed line) are examples of sulfide- and sulfate-saturated experiments respectively. The peaks were background-corrected and converted to relative intensities. The peak for run 54A was smoothed to reduce noise. The inset shows the original profiles in absolute intensities for both measurements. Measurement conditions for the examples shown were identical except for the dwell time.

The sulfur speciation in the glasses from sulfide-saturated experiments ranges from $X(S^{6+}) = -0.05 \pm 0.20$ to $X(S^{6+}) = 0.06 \pm 0.06$ (2 σ). Negative values reflect the scattering of the data around $X(S^{6+}) = 0$ and the larger uncertainty in $X(S^{6+})$ from the counting statistics because of the low sulfur content in these samples. In sulfate-saturated experiments, $X(S^{6+})$ ranged from 0.76 ± 0.05 to 0.92 ± 0.07 with an average of 0.81 ± 0.12 (2 σ).

4. DISCUSSION

Several assumptions are built into the estimation of sulfur speciation using Eqn. 3. First, that the scale assumes that sulfur is present only as a combination of sulfide and sulfate species; second, that the observed shifts in λ SK α are only due to the relative proportions of these two species in the samples; and third, that there is a linear relationship between wavelength shift and the proportions of the two species.

Winther et al. (1998) suggested that other sulfur species such as S₂⁻ and S₃⁻ could be present in silicate melts, and that in those cases the estimated $X(S^{6+})$ values should be more properly considered as mole fraction sulfate equivalents. Paris et al. (2001) used X-ray absorption near edge structure (XANES) to investigate sulfur speciation in one natural and four synthetic glasses and found that no species other than S²⁻ and S⁶⁺ were present. They extrapolated these results to conclude that these are the only two sulfur species present in magmatic systems. However, the synthetic samples showing only sulfate species in Paris et al. (2001) were equilibrated at very high oxygen fugacities: manganosite-hausmannite buffer ($fO_2 = MNO \approx FMQ + 4$), hematite-magnetite buffer ($fO_2 = MH \approx FMQ + 5$), or in air ($fO_2 \approx FMQ + 10$). In contrast, Métrich et al. (2002), also using XANES, found sulfite (S⁴⁺) present in melt inclusions in olivine from Stromboli and Vesuvius (Italy). They estimated the oxidation state of these melt inclusions (from the $Fe^{3+}/\Sigma Fe$ in the glasses) to range between Δ FMQ = + 0.2 and Δ FMQ = + 1.3 (-0.5 to 0.6 log units relative to the Ni-NiO buffer). Additional evidence supporting multiple speciation of sulfur in silicate glasses was presented by McKeown et al. (2004). They used XANES to analyze borosilicate glasses doped with sulfur and found that although glasses synthesized under air contained only sulfate species, less oxidized glasses

Table 2. Run durations, run products, sulfate mole fractions, and fO_2 in the quenched glasses.

Run	t (hr)	Run products ^a	ΔFMQ	$X(S^{6+})$	2σ
52B	4	gl, sulfide, ol, spl	-2.87	-0.05	0.20
54A	4	gl, sulfide, ol, spl	-1.50	0.01	0.16
54B	4	gl, sulfide, ol, spl	-1.54	0.06	0.06
26	4	gl, sulfate, ol, spl, opx, cpx	3.82	0.82	0.10
30B	6	gl, sulfate, ol, spl, opx, cpx	2.59	0.92	0.07
34	4	gl, sulfate, ol, spl, opx, cpx	1.85	0.78	0.07
35A	2	gl, sulfate, ol, spl, opx, cpx	2.41	0.77	0.06
50	4	gl, sulfate, ol, spl	2.22	0.76	0.05
52A	4	gl, sulfate, ol, spl	2.70	0.76	0.15
56A	4	gl, sulfate, ol, spl	2.46	0.90	0.10
56B	4	gl, sulfate, ol, spl	2.50	0.79	0.08

^a gl = glass; ol = olivine; spl = spinel; opx = orthopyroxene; cpx = clinopyroxene.

contained not only sulfate and sulfite, but also S-S doublets and sulfur-polysulfide chains.

The shift in $\lambda SK\alpha$ for different sulfide-sulfate pairs (e.g., FeS-CaSO₄, Carroll and Rutherford, 1988; FeS-BaSO₄, Wallace and Carmichael, 1994; Métrich and Clochiatti 1996; ZnS-BaSO₄, Gurenko and Schminke, 1998, 2000; this work) is highly reproducible (0.30 ± 0.02 PM, 2σ). This indicates that, in general, the variations of $SK\alpha$ among sulfides and among sulfates is negligible. However, sulfides with bianions in their structure (e.g., $(S-S)^{2-}$ in FeS₂ and $(As-S)^{2-}$ in FeAsS) show positive deviations in $\lambda SK\alpha$, resulting in apparent $X(S^{6+})$ ranging between 0.11 and 0.18 (Winther et al., 1998).

Therefore, the ratio obtained by using Eqn. 3 is not a quantitative indicator of the relative proportions of sulfide and sulfate species and should be taken as “sulfate mole fraction equivalent” ($X(S^{6+})_{eq}$), as suggested by Winther et al. (1998). Nonetheless, estimates of “sulfate mole fraction equivalent” provide a framework in which the speciation of sulfur can be estimated and compared.

4.1. Evaluation of Available Models of Sulfur Speciation as a Function of Oxidation State

Wallace and Carmichael (1994) derived an expression to describe the sulfur speciation as a function of oxidation state based on Eqn. 1:

$$\log(X(S^{6+})/X(S^{2-})) = a \log fO_2 + b/T(K) + c \quad (4)$$

where $a = 1.02$, $b = 25,410$, $c = -10$, and $T(K)$ = temperature in Kelvin. According to Wallace and Carmichael (1994), the coefficients “a” and “c” can be obtained from linear regression of the data in Carroll and Rutherford (1988), whereas “b” is the temperature coefficient from the Ni-NiO buffer (NNO) of Huebner and Sato (1970) multiplied by 1.02 (the value of “a”).

Métrich and Clochiatti (1996) and Gurenko and Schminke (1998, 2000) used Eqn. 4 to estimate the oxidation state of magmas from estimates of sulfur speciation. However, this cannot be done directly, because this equation is neither solved for $X(S^{6+})$ nor expressed relative to ΔNNO . Further manipulations and assumptions not shown in Wallace and Carmichael (1994), Métrich and Clochiatti (1996), or Gurenko and Schminke (1998, 2000), are required to derive the appropriate expressions that relate $X(S^{6+})$ to a reference buffer.

Combining the NNO buffer expression (Huebner and Sato, 1970)

$$\log fO_{2(NNO)} = 9.36 - 24930/T(K) \quad (5)$$

and

$$\Delta NNO_{sample} = \log fO_{2(sample)} - \log fO_{2(NNO)} \quad (6)$$

we obtain:

$$\log fO_{2(sample)} = \Delta NNO_{sample} + 9.36 - 24930/T(K) \quad (7)$$

which used in eqn. 4 gives:

$$\log(X(S^{6+})/X(S^{2-})) = 1.02\Delta NNO_{sample} - 18.60/T(K) - 0.45 \quad (8)$$

and converted to a natural logarithmic expression yields:

$$\ln(X(S^{6+})/X(S^{2-})) = 2.35\Delta NNO_{sample} - 42.83/T(K) - 1.04 \quad (9)$$

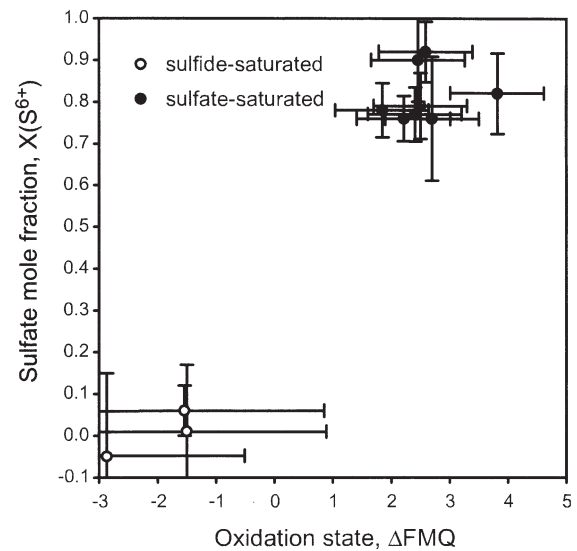


Fig. 3. Sulfur speciation against oxidation state, measured in experimental glasses from this work (2σ error bars).

Because the equilibrium used to derive Eqn. 4 assumes that S^{6+} and S^{2-} are the only possible valence states of sulfur:

$$X(S^{2-}) = 1 - X(S^{6+}) \quad (10)$$

which can be used to solve Eqn. 9 for $X(S^{6+})$:

$$X(S^{6+}) = 1/(1 + \exp(42.83/T(K) + 1.04 - 2.35\Delta NNO)) \quad (11)$$

Eqn. 11 is a sigmoidal function of the form:

$$y = a/(1 + \exp(b - cx))$$

In this case $a = 1$, $b = (42.83/T(K) + 1.04)$, and $c = 2.35$. The effect of the term associated with temperature ($42.83/T(K)$) is small and decreases with increasing temperature. A simplified parametrization of Eqn. 11 can be obtained using a constant $T = 1000$ °C, which is a reasonable magmatic temperature and introduces an error of less than 0.6% in the calculated $X(S^{6+})$ for temperatures between 500 °C and 1500 °C. The resulting equation:

$$X(S^{6+}) = 1/(1 + \exp(1.08 - 2.35\Delta NNO)) \quad (12)$$

solved for NNO:

$$\Delta NNO = 0.43 \ln(X(S^{6+})/X(S^{2-})) + 0.46 \quad (13)$$

is the explicit form of Eqn. 4 used to calculate the oxidation state of primitive melts from determinations of sulfur speciation.

Eqns. 12 and 13 can be translated into FMQ units although some additional considerations are needed because the difference between FMQ and NNO is pressure and temperature dependent (e.g., $NNO = FMQ + 0.70$ at 0.1 GPa and 1000 °C; $FMQ + 0.25$ at 1 GPa and 1000 °C; $FMQ + 0.30$ at 1 GPa and 1200 °C). As a first approximation, and for consistency with available data, a conversion factor of $\Delta NNO = \Delta FMQ - 0.70$ will be used.¹ This is the value used by Wallace and Carmichael (1994) to compare their data (in ΔNNO) to the data of Carroll and Rutherford (1988) (in ΔFMQ) and probably also adopted by Métrich and Clocchiatti (1996), and Gurenko and Schmincke (2000), as inferred from the position of the data from Carroll and Rutherford (1988) in their plots.

Thus, Eqns. 12 and 13 can be expressed in terms of ΔFMQ as:

$$X(S^{6+}) = 1/(1 + \exp(2.73 - 2.35\Delta FMQ)) \quad (14)$$

$$\Delta FMQ = 0.43 \ln(X(S^{6+})/X(S^{2-})) + 1.16 \quad (15)$$

Figure 4 shows all available data on sulfur speciation with independent estimates of oxidation state (Nagashima and Katsura, 1973; Katsura and Nagashima, 1974; Carroll and Rutherford, 1988; Wallace and Carmichael, 1992, 1994; Nilsson and Peach, 1993; Matthews et al., 1999; De Hoog et al., 2004; this work). The curve defined by Eqn. 15 is shown as a solid line.

¹ Note that although $NNO \approx FMQ + 0.7$, $\Delta NNO \approx \Delta FMQ - 0.7$ because of the definition of the delta notation. $\Delta NNO = \log f O_{2(\text{sample})} - \log f O_{2(NNO)}$ and $\Delta FMQ = \log f O_{2(\text{sample})} - \log f O_{2(FMQ)}$; hence, $\Delta NNO = \Delta FMQ + \log f O_{2(FMQ)} - \log f O_{2(NNO)}$. Substituting $\log f O_{2(NNO)} = \log f O_{2(FMQ)} + 0.7$ above yields $\Delta NNO = \Delta FMQ - 0.7$.

The data from Nagashima and Katsura (1973) and Katsura and Nagashima (1974) are problematic. Carroll and Rutherford (1988) and Baker and Rutherford (1996a,b) showed a shift between the data from Na_2O-SiO_2 melts (Nagashima and Katsura, 1973) relative to the data from tholeiitic basalts (Katsura and Nagashima, 1974). They attributed this shift to the notion that alkali-rich magmas favor oxidized forms of S (Stormer and Carmichael, 1971). However, the data from Nagashima and Katsura (1973) and Katsura and Nagashima (1974) overlap and are shifted by about -1.5 log units relative to the rest (dash-dot curve in Fig. 4). We verified and recalculated these data several times and concluded that Carroll and Rutherford (1988) and Baker and Rutherford (1996a,b) likely misplotted them. Thus, the shift in the data from Nagashima and Katsura (1973) and Katsura and Nagashima (1974) cannot be explained by differences in the alkalinity of the melts and the discrepancies between these data and the rest may result from systematic errors in the estimation of oxidation state. Because we could not identify the source of these errors, the data from Nagashima and Katsura (1973) and Katsura and Nagashima (1974) will not be included in subsequent analysis.

The curve derived by Wallace and Carmichael (1994) is constrained by the data from Carroll and Rutherford (1988) because they were the only data on oxidized systems available at the time. Matthews et al. (1999) obtained data from melt inclusions from Lascar volcano and Cerro Overo (Chile) and included data from Nilsson and Peach (1993) to derive a 5th

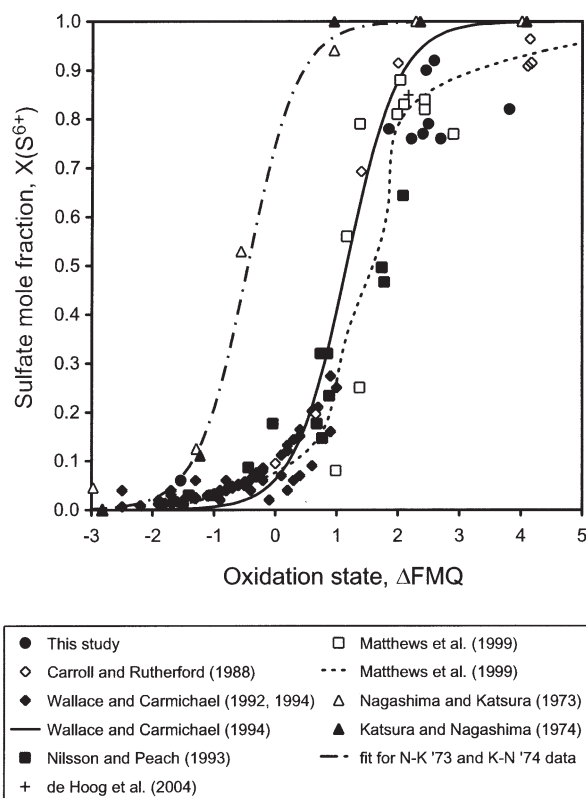


Fig. 4. Available data on sulfur speciation with independent estimates of oxygen fugacity, and speciation models of Wallace and Carmichael (1994) and Matthews et al. (1999).

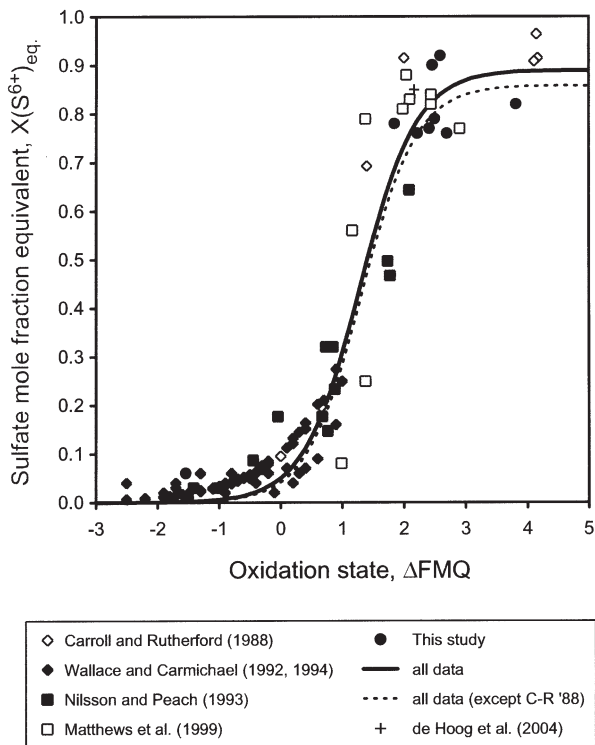


Fig. 5. Available data on sulfur speciation against oxygen fugacity, and the nonlinear regressions derived in this work.

order polynomial fit (dashed curve in Fig. 4) expressing ΔFMQ as a function of $X(\text{S}^{6+})_{\text{eq.}}$.

4.2. Derivation of an Empiric Model for Sulfur Speciation as a Function of Oxidation State

The data obtained in this work complement the available data, especially at high oxygen fugacities where data are scarce. The compiled data were used to derive an empiric model relating sulfur speciation and oxygen fugacity. We take into consideration that the sulfur speciation estimated from EPMA is a sulfate mole fraction equivalent ($X(\text{S}^{6+})_{\text{eq.}}$), which assumes sulfur present only as S^{2-} and S^{6+} .

A nonlinear regression to a sigmoidal curve analogous to Eqn. 14 (solid curve in Fig. 5) was obtained using statistical software (SigmaPlot v.8). The resulting equation:

$$X(\text{S}^{6+})_{\text{eq.}} = 0.89 / (1 + \exp(2.82 - 2.18\Delta\text{FMQ})) \quad (16)$$

fits the data with a correlation coefficient $r^2 = 0.92$.

Because most of the data are from mafic melts (basalts and basaltic andesites) another regression, to test for possible compositional effects, was obtained by eliminating the data from Carroll and Rutherford (1988), which consist of speciation data derived from intermediate to felsic melts (trachyandesites, andesites, and dacites). The equation thus obtained (dashed curve in Fig. 5):

$$X(\text{S}^{6+})_{\text{eq.}} = 0.86 / (1 + \exp(2.89 - 2.23\Delta\text{FMQ})) \quad (17)$$

fits the data with a correlation coefficient $r^2 = 0.91$ and is, in

essence, identical to Eqn. 16, with the exception that the upper asymptotic value is slightly lower (0.86 vs. 0.89).

The asymptotic values for $X(\text{S}^{6+})$ in Eqns. 16 and 17 are consistent with the additional presence of sulfur as sulfite (S^{4+}) in oxidized melts as documented by Métrich et al. (2002). For reference, the apparent $X(\text{S}^{6+})$ for sulfite calculated from SK α data from Kucha et al. (1989) yields $X(\text{S}^{6+})_{\text{eq.}} = 0.80 \pm 0.07$, and De Hoog et al., (2004) estimated sulfur speciation in melt inclusions from Mt. Pinatubo of $X(\text{S}^{6+})_{\text{eq.}} = 0.85 \pm 0.10$.

The relations obtained in Eqns. 16 and 17 indicate that most of the change in sulfur speciation is expected to occur in the range FMQ to $\Delta\text{FMQ} = +2$. Eqn. 17, solved for ΔFMQ (curve in Fig. 6), gives:

$$\Delta\text{FMQ} = 1.30 - 0.45[\ln(0.86/X(\text{S}^{6+})_{\text{eq.}}) - 1] \quad (18)$$

which can be simplified to a linear function in the range $0.2 < X(\text{S}^{6+})_{\text{eq.}} < 0.7$ (thick line in Fig. 6):

$$\Delta\text{FMQ} = 2.28 \times (\text{S}^{6+})_{\text{eq.}} + 0.32 \quad (19)$$

Eqn. 19 could be used as an independent oxybarometer from estimates of $X(\text{S}^{6+})_{\text{eq.}}$. Although the range of application is narrow ($-0.75 < \Delta\text{FMQ} < 1.9$) this is a critical range for the geochemistry of sulfur because it defines the range over which sulfides become unstable and sulfite-sulfate speciation becomes dominant. Outside this range, small uncertainties in $X(\text{S}^{6+})_{\text{eq.}}$ translate into increasingly large uncertainties in $f\text{O}_2$ and the oxybarometer becomes unreliable. However, $X(\text{S}^{6+})_{\text{eq.}} < 0.2$ would indicate $f\text{O}_2 < \Delta\text{FMQ} = +0.75$, whereas $X(\text{S}^{6+})_{\text{eq.}} > 0.7$ would indicate $f\text{O}_2 > \Delta\text{FMQ} = +1.9$. More direct methods (e.g., olivine-orthopyroxene-spinel equilibria) are recommended for the estimation of oxidation states where possible. Additional data with independent estimates of both $f\text{O}_2$ and $X(\text{S}^{6+})_{\text{eq.}}$ would increase the reliability of this approach.

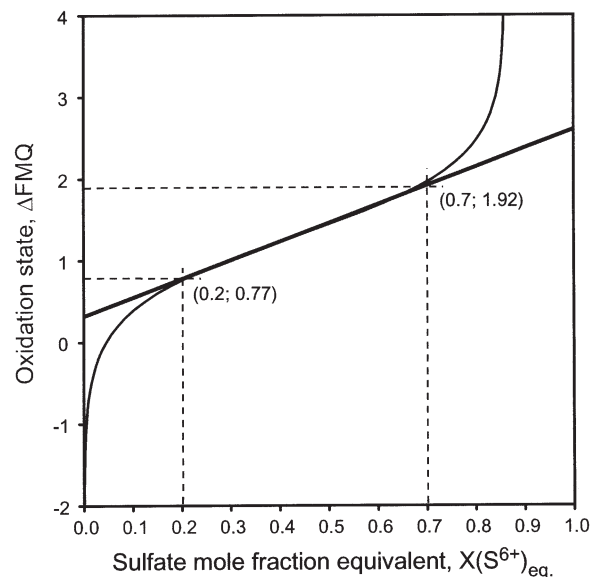


Fig. 6. Oxidation state against sulfur speciation (Eqn. 18). The straight line is the linear fit of the curve in the interval $0.2 < X(\text{S}^{6+})_{\text{eq.}} < 0.7$ (Eqn. 19). Numbers in parenthesis are $X(\text{S}^{6+})_{\text{eq.}}$ and the ΔFMQ calculated from the linear regression).

5. CONCLUSION

The results documented here are consistent with the presence of sulfur as sulfite in addition to sulfate in oxidized silicate melts, as shown by Métrich et al. (2002). Therefore, the peak shift for SK α relative to a sulfide standard determined by EPMA cannot be attributed solely to a combination of sulfide and sulfate species. However, because peak shifts can be determined by EPMA, and the presence of sulfide, sulfite, and sulfate species can only be determined at this point by XANES, the SK α peak shift can be used to estimate "sulfate mole fraction equivalents" ($X(S^{6+})_{eq}$) which can still give a relative indication of the speciation. Nonlinear regressions fit the available data to sigmoidal curves, which are approximately linear over the interval in which most of the change in speciation occurs. This linear function could be used as an independent oxybarometer in this critical transition range of fO_2 , especially for melt inclusions with relatively high sulfur contents.

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